PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C08J 5/18, C08L 3/12, 3/18

A1

(11) International Publication Number: WO 97/33934

(43) International Publication Date: 18 September 1997 (18.09.97)

(21) International Application Number: PCT/US97/03848

(22) International Filing Date: 14 March 1997 (14.03.97)

(30) Priority Data:

60/013,437	15 March 1996 (15.03.96)	US
08/816,929	13 March 1997 (13.03.97)	US

(71)(72) Applicants and Inventors: SPENCE, Orville [US/US]; 819 Wyndham, Arlington, TX 76017 (US). NEVLING, John [US/US]; 17 Hillcrest Avenue, Gladstone, NJ 07934 (US). TORMEY, Beth, C. [US/US]; 17 Ridge Road, Frenchtown, NJ 08825 (US).

(74) Agents: MOORE, Stanley, R. et al.; Jenkens & Gilchrist, P.C., Suite 3200, 1445 Ross Avenue, Dallas, TX 75202-2799 (US).

(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: BIODEGRADABLE SHEET AND METHOD OF MANUFACTURE OF SAME

(57) Abstract

A biodegradable material capable of being formed into a thin sheet is formed for any number of uses according to the method disclosed herein. Clean up of the sheet material is quick, easy and inexpensive since the biodegradable material is water-soluble. Once the sheet material is no longer desired, spraying or otherwise contacting it with water dissolves the material into its constituent components.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

BIODEGRADABLE SHEET AND METHOD OF MANUFACTURE OF SAME

CROSS-REFERENCE TO RELATED APPLICATION

This Application claims the benefit of prior filed and co-pending U.S. Provisional Application Serial No. 60/013,437, entitled "BIODEGRADABLE SHEET AND METHOD OF MANUFACTURE OF SAME", filed March 15, 1996 (Docket No. 27798-31L, Inventors: John Nevling and Orville Spence).

TECHNICAL FIELD

The present invention relates to biodegradable materials and methods for manufacture of same, and more specifically, to a biodegradable material capable of being formed into a thin sheet and method for producing the same.

BACKGROUND OF THE INVENTION

Many types of biodegradable materials are known in the art. One of the more common and commercially successful biodegradable materials are comprised of starch-based compounds. Typically, these compounds are comprised of one or more modified high-amylose starch components. Dyes and other additives can be used to impart desired characteristics such as color and texture, for example. High amylose starches are used to impart resilience and compressibility to the material. The addition of polyvinyl alcohol ("PVA") is also known to increase the flexibility of starch-based biodegradable materials.

Starch is a polysaccharide typically comprising a mixture of about 20-25% amylose and about 75-80% amylopectin which is organized into compact granular structures. Amylose is a linear polymer of D-anhydroglucose units which are linked by alpha-1,4-D-glucosidic bonds. High-amylose starch is starch containing at least 45% by weight amylose content. Modified starch is starch derivatized or modified by processes known in the art, such as etherification with alkylene oxide.

Starch-based biodegradable materials are typically produced by mixing one or more components to form a material. Subsequently, the material is extruded and then

cut, milled, shredded or otherwise formed into one or more shapes and/or sizes. While traditional die extruders are typically used, heretofore it has been difficult to extrude the biodegradable material to a form less than 1/8" in thickness. Thus, the uses for starch-based biodegradable materials have been limited by this lower limit size restriction. For example, thin sheets of starch-based biodegradable materials of less than about 1/8" in thickness have not been available. Sheets of biodegradable materials would have a myriad of uses. For example, paper products such as writing paper and stationary could be formed of a biodegradable material and used for the communication of sensitive or confidential information. Once the information printed on the sheet was utilized, the sheet could be brought into contact with a sufficient amount of moisture (water, urine, saliva, etc.) to dissolve the paper into its constituent components, permanently and completely disposing of the information printed on the sheet. Many other examples of uses for a biodegradable thin sheet exist.

Thus, the background of starch-based biodegradable materials does not suggest that such starch-based materials can be shaped to form a thin sheet of useful thickness as paper or like product and a need remains for a biodegradable material capable of existing in a thin sheet form, such sheet capable of use as any other sheet of material.

SUMMARY OF THE INVENTION

The present invention provides a starch-based biodegradable material capable of being formed into a thin sheet of thicknesses of less than 1/8", preferably less than 1/16" and particularly between 1/32" and 1/64". Sheets having thicknesses as small as 1/200" can be produced. A sheet of biodegradable material capable of existing at these thicknesses and a method for the production of the same was discovered by the inventors of the present invention in the classical context of an unintended result of experimentation. The inventors of the present invention were experimenting with the introduction of certain additives to a starch-based biodegradable material to improve the flexibility of the material when its was discovered that the addition of a certain concentration of polyvinyl alcohol ("PVA") causes the resultant starch-based material to extrude in a manner which forms a sheet of the material of thickness of between 1/32" and 1/64". The inventors replicated the experiment several times and

each time produced the thin sheet of biodegradable material. Immediately recognizing at least one application for such a sheet material, the inventors cut a section of the thin sheet biodegradable material having the approximate dimensions of 8 ½" x 11", the size of a standard sheet of paper. The sheet was then fed through a standard printer and the resultant printed sheet appeared virtually identical to a standard piece of bond paper. The sheet received the ink and accepted both colors and black type. The flexibility of the sheet approximates that of standard writing paper.

As with other paper products, the resultant sheet material can be colored using dyes, if desired. Unlike other paper products, however, the biodegradable sheet of the present invention can be easily disposed of in a manner which is easy, inexpensive, permanent and environmentally safe. Indeed, while not recommended, especially if no-food grade dyes or other additives are present, the sheet could be disposed of by being consumed by a human. This feature is particularly useful, for example, in children's books where accidental consumption of the pages of the book would not be harmful to a child.

Printing on and handling of the sheet material has been tested and the sheet material has been found to behave much like traditional bond or fiber paper in that it is flexible, readily accepts inks, does not smear or require abnormal drying times, and is durable. The sheet material is formed from a renewable source, however, and, unlike traditional bond or fiber papers, is easily dissolved into its constituent components upon prolonged exposure to moisture and is environmentally safe.

BRIEF DESCRIPTION OF THE DRAWING

For a more complete understanding of the present invention and the advantages thereof, reference is now made to the following description taken in conjunction with the accompanying drawing in which:

FIGURE 1 is a flowchart illustrating the steps of the method of manufacturing the biodegradable sheet material of the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

Referring to FIGURE 1, there is shown the steps of the method of manufacturing the biodegradable sheet material of the present invention.

The process preferably includes the use of a continuous extrusion process using extruders known in the art. In a preferred embodiment, an intermeshing, self-wiping, co-rotating, twin screw extruder is utilized in the process. Since the advantageous physical properties of the biodegradable sheet material of the present invention depend in part upon proper and complete mixing of the raw components, exact feeding, mixing, heating and cooling within the process is important to the process. Although an intermeshing, self-wiping, co-rotating, twin screw extruder is described, it should be noted that any appropriate type of extruder, such as a single screw type extruder for plastic, can be utilized.

First, if color is desired, food grade dyes and/or colors are provided in preferable amounts of between 0.01% and 2% in step 10. Food grade dyes are selected since the resultant sheet material is biodegradable, although other dyes could be used, if desired. In the event color is added, the percentage amounts of the additional components are adjusted accordingly. In step 20, from between 0% and 20% of modified or unmodified starch is provided. Next, high amylose modified starch is provided in a range of between 60% - 90% by weight in step 30. The foregoing components are preferably provided in their dry form. The starch may be modified or derivatized via processes well known in the art, including without limitation, etherification, esterification, oxidation, acid hydrolysis and crosslinking. Etherification with up to 15% by weight of alkylene oxide containing 2 to 6 carbon atoms is a preferred modification technique. The modified starch is preferably a high-amylose starch of approximately 70% amylose content modified with propylene oxide.

In step 40, from between 8 % and 20% by weight, and preferably between 10% and 15% of polyvinyl alcohol is provided as a component. Although a biodegradable material capable of being formed into a sheet is produced throughout the range of PVA listed above, the optimum percentage observed is between 12% and 12.5%. Any polyvinyl alcohol may be used, with the hydrolyzed or substantially hydrolyzed

polyvinyl alcohols being preferred. A substantially hydrolyzed PVA, for example, Airvol 325™ by Air Products and Chemicals, Inc. of Irving, Texas, is used. Airvol 325™ is fully hydrolyzed (98.0%-98.8%) and has a viscosity of 28.0 - 32.0 cps (a 4% aqueous solution at 20°C) and a pH of between 5.0 - 7.0.

In the next step of the process, step 50, the components are mixed in the extruder along with water. The total moisture content of the starch in the extruder may be 25% or less by weight based upon the dry weight of the starch, and preferably between about 10% to 21% by weight. Total moisture content includes both residual moisture of the starch and water fed to the extruder. Typically, starch contains about 9% to 12% residual moisture. The resultant mixture is then heated to a temperature of between about 88°C (190°F) and 250°C (482° F), preferably between about 100°C (212°F) and 205°C (400°F) within the extruder while being conveyed, kneaded, sheared and extruded using a die as in step 60. Much of the heat is provided by pressure exerted on the material by the extruder during these steps. These steps are preferably performed by a continuous process extruder, but could be achieved manually, if desired. Due to the unique formulation of the biodegradable material, the extrudate balloons out of the die, forming the thin sheet size of the biodegradable material of less than 1/8".

In step 70, the extrudate is optionally cut or slit and pressed to a desired size(s) and shape(s) and allowed to cool. These step of the process can likewise be accomplished by one or more of any means known within the art.

Although the modified high-amylose material exhibits good expansion characteristics, unmodified or modified starches with lower amylose concentrations can be added (in approximately 0-20% levels) to aid in the expansion characteristics of the material. High-amylose starches are used to impart resilience and compressibility to the biodegradable material. Flexibility and other properties, if desired, can also be achieved through additives. Preferably, the material has a specific density of from approximately 0.5 to 40 lbs/ft^3, and more particularly, from about 0.5 to 20 lbs/ft^3.

Once formed according to the present invention method, the biodegradable sheet material can be used in a number of ways.

Importantly, the biodegradable sheet material of the present invention can be used without prior planning and concern of clean up once its disposal is desired. The water-soluble biodegradable sheet material dissolves upon contact with water, thereby making clean up a simple process of bringing water into contact with the sheet material.

Although preferred embodiments of the invention have been illustrated in the accompanying drawing and described in the foregoing Detailed Description, it will be understood that the invention is not limited to the embodiments disclosed, but is capable of numerous rearrangements and modifications of parts and elements without departing from the spirit of the invention.

WHAT IS CLAIMED IS:

1. A biodegradable sheet, comprising:

a high amylose starch component;

from about 8% to 20% by weight of polyvinyl alcohol; and

said sheet having a thickness of less than 1/8".

2. The biodegradable sheet of Claim 1, wherein the amylose starch component contains at least 45% by weight amylose.

3. The biodegradable sheet of Claim 2, wherein the amylose component is further modified with up to 15% by weight of alkylene oxide containing from between 2 and 6 carbon atoms.

4. The biodegradable sheet of Claim 2, wherein the amylose component is further modified with from about 10% to 15% by weight of polyvinyl alcohol.

5. The biodegradable sheet of Claim 4, wherein the starch component contains at least 70% by weight amylose.

6. The biodegradable sheet of Claim 2, wherein the starch component is modified with propylene oxide.

7. The biodegradable sheet of Claim 4, wherein the polyvinyl alcohol is hydrolyzed or substantially hydrolyzed.

8. The biodegradable sheet of Claim 1, wherein the sheet comprises from about 60% to 90% by weight of the starch component.

9. A biodegradable sheet, comprising:

a high amylose starch component;

from about 8% to 20% by weight of polyvinyl alcohol;
said sheet having a thickness of less than 1/8"; and
said sheet being printable.

10. The biodegradable sheet of Claim 9, wherein the sheet is printed with ink.

11. The biodegradable sheet of Claim 9, wherein the starch component contains at least 45% by weight amylose.

12. The biodegradable sheet of Claim 11, wherein said starch component is further modified with up to 15% by weight of alkylene oxide containing 2 to 6 carbons.

13. The biodegradable sheet of Claim 9, wherein the starch component contains at least 70% by weight amylose.

14. The biodegradable sheet of Claim 13, wherein the starch component is further modified with propylene oxide.

15. The biodegradable sheet of Claim 14, wherein the starch component is further modified with from about 10% to 15% by weight of polyvinyl alcohol.

16. A method for forming a biodegradable sheet having a thickness of less than about 1/8", comprising the steps of extruding a composition comprising a high amylose component and from about 8% to 20% by weight of polyvinyl alcohol in the presence of a total moisture content of from about 25% or less by weight and at a temperature of from about 88°C to 250° C.

17. The method of Claim 16, wherein the starch component contains at least about 45% by weight amylose.

18. The method of Claim 17, wherein the starch component is further modified with up to about 15% by weight of alkylene oxide containing from 2 to 6 carbon atoms.

19. The method of Claim 17, wherein the starch component is further modified with from about 10% to 15% by weight of polyvinyl alcohol.

20. The method of Claim 16, wherein the starch contains at least 70% by weight amylose and is further modified with propylene oxide.

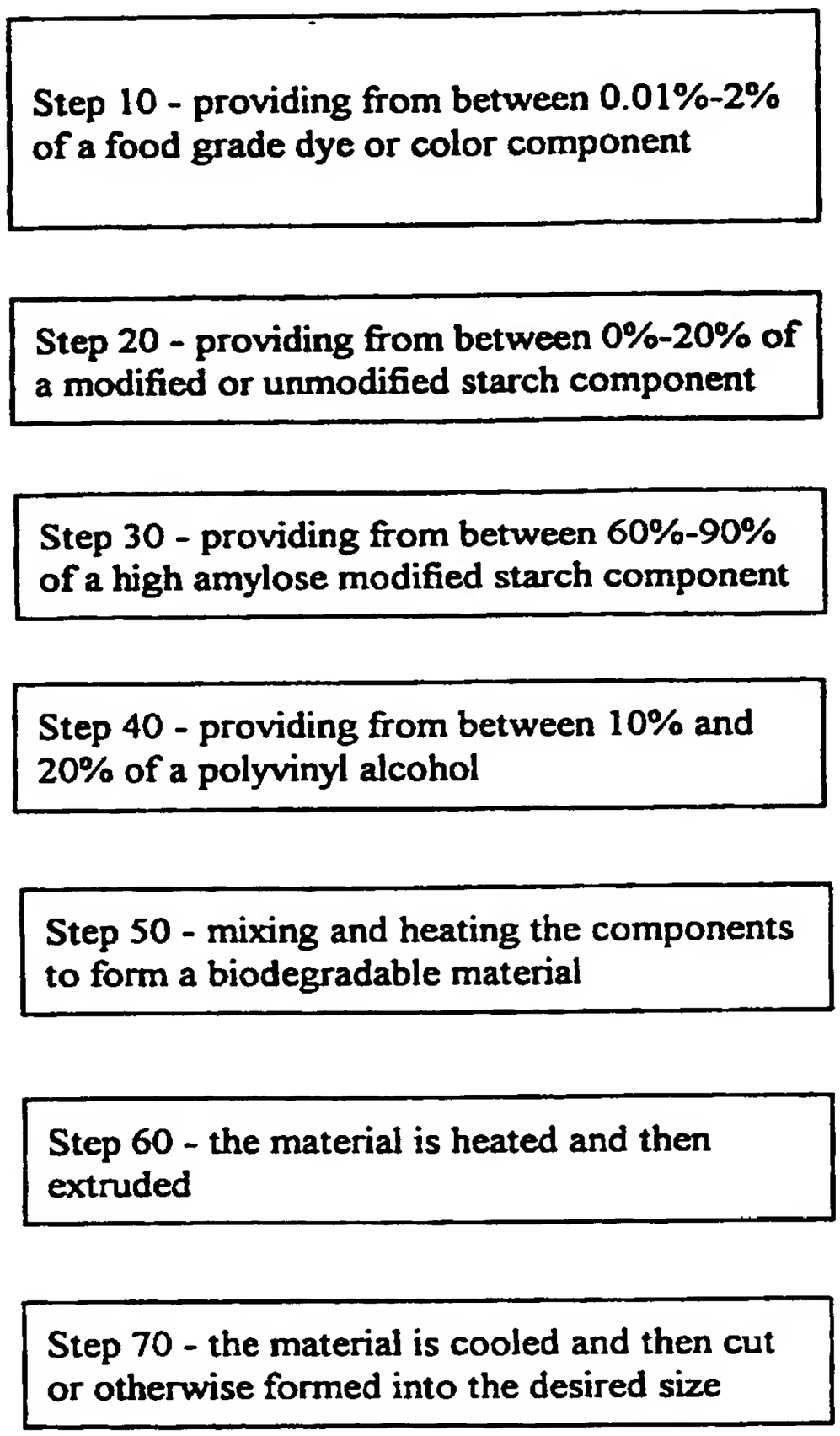
Step 10 - providing from between 0.01%-2% of a food grade dye or color component
Step 20 - providing from between 0%-20% of a modified or unmodified starch component
Step 30 - providing from between 60%-90% of a high amylose modified starch component
Step 40 - providing from between 10% and 20% of a polyvinyl alcohol
Step 50 - mixing and heating the components to form a biodegradable material
Step 60 - the material is heated and then extruded
Step 70 - the material is cooled and then cut or otherwise formed into the desired size

FIGURE 1

INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 97/03848

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J5/18 C08L3/12 . C08L3/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 312 641 A (AUSTIN H. YOUNG) 4 April 1967 see column 2, line 15 - line 17 see column 2, line 6 - line 9 see example V; tables I,,II,,III -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 May 1997	25. 06. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Lensen, H

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No
PCT/US 97/03848

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3312641 A	04-04-67	BE 648676 A	01-10-64
		DE 1745680 A	09-09-71
		FR 1419629 A	18-02-66
		GB 1075002 A	
		NL 6406933 A	21-12-64
		SE 313918 B	25-08-69
		US 3314810 A	18-04-67